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An H plasma has a remarkable effect on dislocation mobility in silicon, reducing its activation energy to 1.2 eV. Applying density functional theory to the interactions of H and H_2 with the core of the 90° partial dislocation in Si, we have identified a path for motion involving kink formation and migration at hydrogenated core bonds which conforms exactly to the experimentally measured activation energy.

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Substantial progress has been made in the study of dislocations in Si culminating in elegant experimental measurements of dislocation mobilities of small segments in Si films [1,2] and high-resolution transmission electron microscopy measurement of kink dynamics [3]. Theory has matched these developments with first-principles calculations of the parameters for dislocation motion [4–6] and broad quantification [7,8] of early hypotheses for the nature of kinks, reconstruction, and dislocation motion [9–11]. Although silicon is the simplest high lattice friction solid, the complexity of dislocation cores on the atomic scale has so far frustrated a consensus on exactly how dislocations move. It is known that the velocity v is thermally activated following

$$v = v_0 \exp(-E/kT),$$

and following Hirth and Lothe [12] it has been widely believed that the exponent arises from a combination of kink formation and migration energies ($E = F_k + W_m$) for segments long enough to guarantee kink lifetime is limited by kink-kink annihilation.

It is not the purpose here to explore the merits and shortcomings of this model, but to focus attention on a newly reported and remarkable effect of H on dislocations, which is important for two reasons. Firstly, because the effect is large, reducing the activation energy for motion by 1 eV, and, secondly, because our understanding of H in Si is crucial to the "smart-cut" process for silicon-on-insulator technology [13].

It is known that electronic deep levels associated with dislocations are passivated by H [14] and that the flow stress of silicon single crystals is reduced by irradiation with H plasma [15]. More recently it has been shown that the glide mobility of individual dislocations is enhanced by the presence of H. Between 390 °C and 480 °C, under an applied shear stress of 68 MPa, it was found that, without H plasma, $v_0 = 7 \times 10^5$ ms^{-1}; $E = 2.2$ eV; however, with H plasma, $v_0 = 2$ ms^{-1}; $E = 1.2$ eV [2]. The effect depended on a 1 h 470 °C or 530 °C prehydrogenation step rather than the H plasma treatment itself, and it was suggested that this enhanced motion was thus different from the flow stress effect [15] and that the pretreatment introduces H as some complex in or near the dislocation which is stable at temperatures below 480 °C. In this paper we consider that both the plasma treatment and the breakup of the H complexes arising from pretreatment cause a flux of H toward the dislocation line. It is known that, at high temperatures, H is in atomic form and, at room temperature, is in molecular form—there is uncertainty as to its nature at the temperature of this experiment, so our modeling starts with the premise of atomic H, but embraces the possible mechanisms of H_2.

Here we use AIMPRO, a self-consistent density functional code running at local spin density approximation (LSDA) level [16]. Norm-conserving pseudopotentials [17] are used except for H. Molecular wave functions consist of n s-, p_x-, p_y-, and p_z-symmetry Gaussian functions; the valence charge density is modeled by m s-functions. The values of (n, m) used here are Si (4,5), H (2,3). The large cluster results were repeated with H (3,4) for nonsurface H and all resulting energy changes were found to be less than 0.1 eV. This was also found to be the case for calculations employing bond-centered orbitals, which effectively introduce some Si $3d$ character into the basis. Structural optimization to negligible forces was by conjugate gradient algorithm. At this stage we have not taken into account the quantum behavior of the proton, and look only for classical trajectories and energy surfaces. The method has been previously successfully applied to dislocations in Si [18] and O_iH_2 [19]. Calculations have been performed with $Si_{134}H_{98}$ clusters unless otherwise stated. The hydrogenated soliton (H-soliton) migration barrier along the dislocation core was calculated in a $Si_{104}H_{82}$ cluster. For H in pure Si, $Si_{95}H_{86}$ was used.

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Primary dislocations in Si are the 60° mixed dislocations and screw dislocations oriented along ⟨110⟩ and lying in {111} slip planes. These dissociate, respectively, into a 90° and a 30° partial and into two 30° partials, separated by a stacking fault of approximate width 50 Å when in equilibrium, generally believed to lie in the glide plane [20]. In detail it has been found that the mobility of a partial depends on whether it is leading or trailing, and on whether it is a 90° or a 30° partial [21], but these are attributed to variations in the activation energies of less than 0.1 eV—comparable with LSDA uncertainties. A single period (SP) structure is studied here on the assumption that, if the double period (DP) structure is indeed lower in energy than SP [18,22], the SP structure will still be favored under an applied stress which causes neighboring kinks of the DP structure to annihilate.

Depending on the reconstruction, a 90° partial dislocation core has a phase which may be labeled either "right" (R) or "left" (L). At the interfaces between two phases there exist antiphase defects, or *solitons* [11]. We find a soliton formation energy of 1.4 eV (improving by cluster size and basis per atom on an earlier AIMPRO calculation which found 1.2 eV [23]) and confirm recent tight binding calculations which gave a soliton formation energy of 1.31 eV [24].

Solitons can migrate rapidly along the dislocation line, and it has been suggested that they mediate both kink formation and propagation [11]. A soliton consists of an undercoordinated Si atom with a deep gap dangling bond state (the structure is that of Fig. 1a without the H atom). It can migrate along the dislocation line (saddle point of Fig. 1b without H), for which we obtain a barrier of 0.15 eV (Fig. 2), while tight binding gave 0.04 eV [24]. The soliton can also begin the process of kink-pair nucleation (Fig. 1d without H) for which we obtain a barrier of 0.29 eV (Fig. 2) and a formation energy of 0.11 eV for the incipient kink pair.

Now we turn our attention to H, which can exist in the Si lattice in a variety of forms. These include H_2 molecules at the tetrahedral (T) site [25], isolated H atoms lying bond centered (H^+_{BC}, H^0_{BC}) or antibonding (H^-_{AB}, H^0_{AB}) [26], as well as H^*_2 [27] (H_{BC} and H_{AB} in neighboring sites). The relative stabilities of these structures have been determined by various groups with H_2 and H^*_2 vying for most stable structure; our relative energies for these structures are given in Table I. Ultimately, supersaturation of H results in platelet formation [28] and, at elevated temperatures, effusion of H_2.

At a 90° partial dislocation it might be expected that H and H_2 favor the enlarged (reconstruction) bonds, possibly breaking them, and H_2 the large channels in the dislocation core. In general they may both be caught in the long-range strain field of the dislocation (forming a Cottrell atmosphere), but given their high mobilities this atmosphere will not likely slow the dislocation motion.

Here we discuss the H-plasma effect in terms of a flux of H atoms (i.e., H_{BC}) on the dislocation line, arriving from the local source of H created by the pretreatment. We note that (i) H_2 gas heated with Si enters as atomic H and (ii) that the elimination of H from the reservoir at 500 °C implies an activation energy 3.6 eV [2], which most likely equates with the loss of atomic H. Furthermore, studies of H-plasma-treated dislocated silicon [29] reveal that dislocations act primarily as recombination centers for H atoms—a process which can be well understood from the results of our calculations. The dislocation has a substantial cross section from the linear extent of the dilatational part of its strain field and, once trapped at the core, H atoms, as we will show later, are mobile along the core so must meet and recombine.

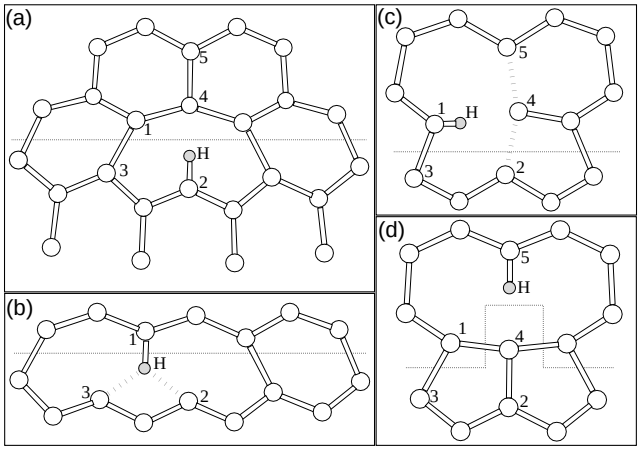

FIG. 1. (a) Structure of H soliton in 90° partial dislocation in Si. (b) Saddle point to motion along the core. (c) Metastable state in motion perpendicular to core. (d) H-kink pair, 0.19 eV more stable than (a). Numbers are referred to in the text. The plane of the page is (111), left/right is $\langle 1\bar{1}0\rangle$ and up is $\langle 11\bar{2}\rangle$. Dislocation axis is shown as a broken line.

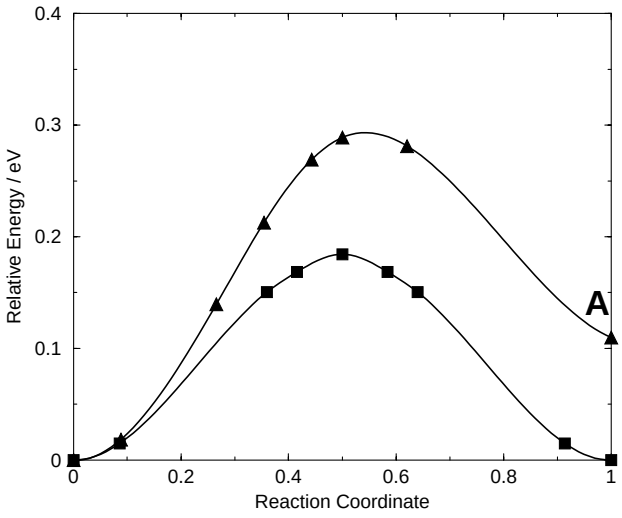

FIG. 2. Barrier to soliton motion in a 90° partial dislocation, (■) along the core, and (▲) perpendicular to the core forming a kink pair. A = kink pair.

TABLE I. Energies of H complexes in Si.

Location of H	Relative Energy/eV per H atom This work	Previous
$(H_2)_T$	0.00	0.00
H_2^*	+0.18	+0.2 − 0.4 [33], +0.2 [34], +0.4 [35], −0.49 [36], −0.34 [37]
2 isolated H^0_{BC}	+2.39	+1.62 [35], +1.6 [33], +2 ± 0.5 [26], +2.7 [33], +3.3 [34]

Our results are summarized in Table II. First we note that H^0_{BC} binds strongly to a neutral soliton with an energy of 2.56 eV (giving structure of Fig. 1a) and to a soliton kink pair by 2.86 eV (giving Fig. 1d). Nucleating a kink pair at a free soliton costs 0.11 eV, while doing so at a H soliton releases 0.19 eV, due to reduced steric effects for the H in the kink pair. Thus H flux may be expected to spontaneously nucleate soliton pairs (of energy 2.8 eV) and, simultaneously, kink pairs, i.e., a complex of a H soliton with a reconstructed kink pair will be formed in addition to a non-H soliton, which will migrate rapidly until it combines with another incoming H atom.

The steady state motion of the dislocation will be controlled by the formation and motion of kinks by these H solitons (Fig. 1a), for which we calculate barriers to motion and kink formation.

Free soliton migration was obtained by relaxing all degrees of freedom, subject to the single constraint (1) below,

$$r^2_{1-3} - r^2_{1-2} = C_1\,, \tag{1}$$

$$r^2_{2-H} - r^3_{3-H} = C_2 \tag{2}$$

(where r_{a-b} is the bond length between atoms a and b from Fig. 1) and locating the maximum in $E(C_1)$ (which was at $C_1 = 0$). With H, the additional constraint (2) had to be applied. Varying C_1 and C_2 independently generates a two-dimensional surface from which a barrier of 1.05 eV is deduced (Fig. 3a). The saddle point structure for motion along the core consists of H bonded to the central Si atom number 1 (Fig. 1b).

Kink-pair formation involves H-soliton motion perpendicular to the line, for which we first found an intermediate structure by relaxing several suitable midpoint candidates and selecting the one with the lowest energy (Fig. 1c). This is an unconstrained metastable structure—the minimum in Fig. 3b. Other points on the left of this figure were then obtained by interpolating between the intermediate structure and the starting structure. At each step the system was fully relaxed in all directions *orthogonal* to the translation vector between the initial and intermediate structures. The second half of the motion was similarly determined by constraining orthogonal to the vector between the intermediate and final structures (Fig. 1d). From Fig. 3b it can be seen that the rate-limiting step for kink-pair formation at a H soliton will be 1.16 eV.

Further expansion of the kink pair can be achieved by similar steps, i.e., rebonding atoms 1–5 and H–3, etc. [11]. The rate controlling step will then be the H-catalyzed kink migration steps, which experience indicates have activation barriers closely similar to the first step, yielding an overall activation energy for motion of 1.16 eV, in

TABLE II. Results from 231 atom clusters.

Structure	Energy (eV)	
Soliton Migration Barrier	without H	with H
Along dislocation core	0.15	1.05[a]
Initiating kink pair	0.29	1.16
Formation energy compared to soliton		
Soliton: kink pair	+0.11	−0.19
Formation energy compared to 2H in same dislocation bond		
Two H solitons separated by single core bond		+0.76
H_2 molecule in sevenfold core ring		+0.96
H_2 molecule at interstitial T site		+1.25

[a]Indicates 186 atoms.

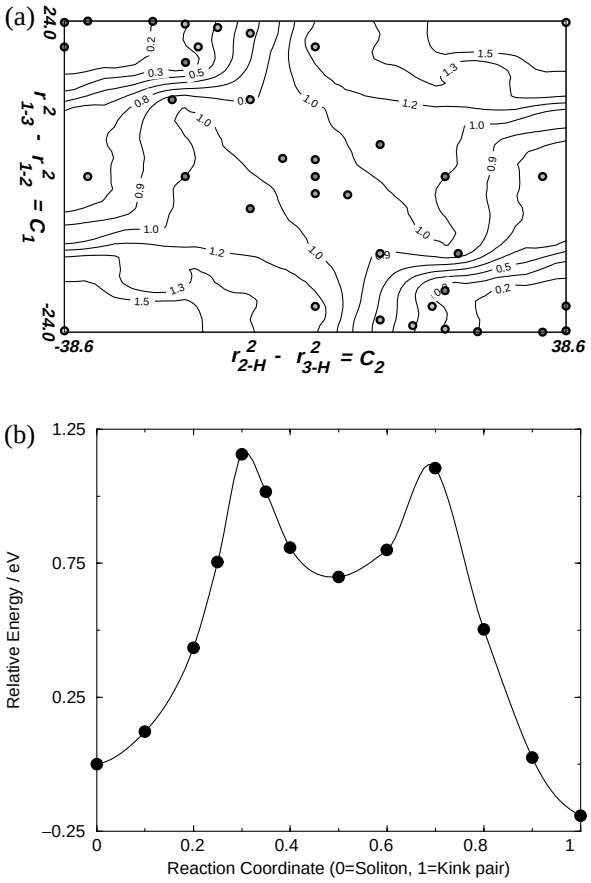

FIG. 3. Barrier to H-soliton motion in a 90° partial dislocation. (a) Along the core: Stable H soliton, top-left and bottom-right; saddle point at $C_1 = C_2 = 0$. (b) Perpendicular to the core forming a kink pair. Dots mark points sampled.

remarkable agreement with the experimentally measured 1.2 eV [2]. The low prefactor, dependent on the H concentration, arises from the low mean-free path of H-soliton-kink complexes under a substantial flux of H atoms.

For comparison, the activation energy for dislocation motion in intrinsic silicon by the soliton mechanism includes the thermal equilibrium concentration of solitons and has an activation energy of at least 1.8 eV [30]. The alternative mechanism invoking fully reconstructed kinks [31] has been found to have an activation energy of 1.8–1.9 eV [24,30], within Hirth-Lothe theory, in disagreement with 1.2 eV obtained by applying the same theory to other recent results [32]. Experimental measurements are in the region of 2.2 eV [2]. If, as has been speculated recently [3], obstacles limit dislocation motion in silicon, then we postulate that in H-catalyzed motion these obstacles either are released by the passage of the free soliton or are etched away by H.

It is possible that a mechanism invoking H_2 molecules is involved, more especially at lower temperatures, and we found clear evidence that H_2 is attracted to the large channel of the dislocation core, being 0.29 eV lower in energy than interstitial H_2. Once there, the molecule can insert *exothermically* into a reconstruction bond, releasing 0.96 eV. The pair of H-soliton complexes thus created can move apart and catalyze kink formation and migration (albeit endothermically by 0.76 eV in the first step).

At higher temperatures, H-soliton complexes readily move together to form intimate pairs and, although the elimination of an H_2 molecule is endothermic, entropy will drive its formation and thus explain the role of dislocations as recombination centers for H atoms in Si [29].

In conclusion, we have presented a mechanism for the strong effect of H plasma on dislocations in silicon, yielding an activation energy for motion conforming closely to that experimentally measured. While there is a fine balance between hydrogen as atoms and as molecules over the temperature range which spans the experimental measurements, it is likely that both forms of H can lead to dislocation motion controlled by the steps presented here.

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